

INDUSTRIAL USE OF CORN STARCH¹

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Introduction

Current domestic consumption of corn starch products, including unmodified and modified starches, in industrial or nonfood applications, amounts to approximately 3 billion pounds per year. About 90% of this volume is accounted for by starch products used as sizing agents and adhesives in making and coating paper and paperboard; as sizes in the manufacture of textiles; and as adhesives in producing boxboard, insulation board, paper bags, cardboard cartons, and gummed labels and tapes. Each of these areas of application has been covered in one or more reviews within the past few years (1-8). The objectives here are to condense and update this literature, to mention a number of other uses, and to discuss some industrially promising developmental products.

Principal Starch Products Used Industrially

Unmodified starch in addition to being useful in various applications is an excellent raw material for making many other industrial products. It is relatively inexpensive and can be partially depolymerized and derivatized readily, only relatively low levels of modification are needed to alter its properties significantly, and all of the important industrial processes can be conducted in the dry state or in aqueous media. Except for enzyme-modified starches, most of which are prepared on-site by the user and not isolated, and pregelatinized starch, the other major industrial grades of modified starch made by aqueous processes can be isolated readily by filtration. This is possible because the reactions proceed well at temperatures below the range where starch granules swell, become sticky, and start to dissolve.

For many industrial applications, starch products are needed that are less viscous, form more stable pastes, and have greater affinity for natural and synthetic fibers or other substrates than does unmodified starch. These properties are achieved through degradative and substitutive reactions applied singly and in selected combinations to starch. Starches considered in this review are either regular unmodified corn starch or products derived from it unless otherwise noted. The types and amounts of the principal starch products sold for industrial uses are given in Table I.

Sales rather than consumption figures are given in Table I because much of the unmodified starch that is sold is processed in-plant by the user to reduce its viscosity to appropriate levels for various applications. The processes most commonly used are enzymatic hydrolysis (9) and steam-jet cooking (10).

TABLE I. SALES OF CORN STARCH PRODUCTS FOR INDUSTRIAL APPLICATIONS IN 1972

Starch Product	Millions of Pounds ^a
Unmodified starch	1,817
Acid-modified starch	340
Oxidized starch	166
Dextrins	150
Cationic starches	100
Pregelatinized starches	100
All others including hydroxyethylstarch	420
Total	3,093

^aData were obtained from starch suppliers. Waxy maize and high-amylose starch sales which are quite small compared to sales of ordinary corn starch are included in the figures.

The preparation and properties of all the modified starches listed in Table I have been reviewed recently (11-16) and are described only briefly here to provide background for subsequent sections on industrial utilization.

Acid-Modified Starches

Detailed descriptions of industrial processes for manufacturing acid-modified starches have not been published; however, methods approximating those used industrially have been described (11).

In essence, acid modification involves heating a fairly concentrated slurry of starch in dilute hydrochloric or sulfuric acid at 50-55°C until the desired degree of conversion is achieved. At this stage, the reaction is terminated by neutralization, then the product is recovered on a filter, washed with water, and dried. The course of the reaction is usually followed by determining the fluidity of samples removed from the reaction at various intervals.

Fluidity is the inverse of viscosity and is expressed as a number defined as follows: A fluidity number corresponds to the number of milliliters of a solution of 5 g. of test product, dissolved in 100 ml. of 0.9% sodium hydroxide, that flows through a

specially designed funnel in 70 sec. at 25°C. Under these test conditions, water has a fluidity of 100 and that of unmodified starch is on the order of 1 (17). Acid-modified starches are often referred to as fluidity starches and are available in several fluidity grades ranging from 20 to 90. The extent of depolymerization associated with various fluidity grades of acid-modified starch is indicated from intrinsic viscosity values of 1.55, 1.05, 0.90, and 0.50 deciliters per gram reported (18) for unmodified corn starch and 20, 40, and 75 fluidity grades, respectively.

Hot pastes of acid-modified starches are much thinner than pastes of unmodified starch at the same solids content. For this reason, acid-modified starches as well as other partially depolymerized starches are often called thin-boiling starches. The gelling power, defined as the ratio of cold paste viscosity to hot paste viscosity (11) is much greater for acid-modified starches than for unmodified starch. The viscosity, film forming, and adhesive characteristics make acid-modified starches useful as warp sizes in textile manufacturing and in certain paper-sizing applications. Acid-modified starches also serve as starting material for the preparation of thin-boiling starch derivatives.

Dextrins

Three major types of dextrins--white dextrins, yellow dextrins, and British gums--are commercially available.

White dextrins are made by heating starch in the presence of moisture under fairly acidic conditions at temperatures ranging from 95° to 120°C (12). Under these conditions hydrolytic breakdown is the principal reaction; consequently, properties of the products resemble those of acid-modified starches. The white dextrins are used in adhesives and in some types of textile finishes.

Yellow dextrins are made by heating starch at low moisture content and moderate acidity at temperatures from 150° to 190°C. The initial depolymerization which takes place is followed by rearrangement and repolymerization to give highly branched starches which do not retrograde easily (associate in solution to insoluble aggregates). The yellow dextrins are the most highly converted, i.e., depolymerized, products among the modified starches. Their degree of polymerization (D.P.) is approximately in the range of 20 to 50 (1). Because of their low D.P., it is possible to make fairly free flowing solutions or pastes which contain up to 60% solids. These pastes are very sticky and dry rapidly because of their high solids content. These properties make the yellow dextrins very useful in adhesive applications which constitute their principal use.

British gums are made by heating starch of very low moisture content to 150° to 190°C with little or no acid present (1). Under these conditions, rearrangement is favored but some hydrolytic breakdown occurs. Because of the high degree of branching in the products, their aqueous dispersions are relatively stable. The British gums are available in a wide range of viscosities and vary in color from light tan to dark brown. Their aqueous dispersions are gummy and spread well, properties which make them useful in a variety of adhesive applications.

Oxidized Starch

Sodium hypochlorite is usually used in the commercial production of thin-boiling oxidized starches. Oxidation is conducted by treating an aqueous alkaline slurry of starch in granule form with sodium hypochlorite solution containing 5 to 10% available chlorine at temperatures usually in the range of 21° to 38°C (13). On completion of the oxidation, the reaction mixture is neutralized with acid, bisulfite solution or sulfur dioxide is added to destroy any unspent oxidant, and the reaction mixture is diluted with water. The product is recovered on a filter, washed with water, and dried. Hypochlorite oxidized starches are available in about the same viscosity range as the acid-converted starches.

Hypochlorite oxidation, in addition to cleaving the starch chains, also introduces a few carboxyl and carbonyl groups into the starch molecules. In commercial products, the degree of substitution (D.S.) defined as the average number of substituents per anhydroglucose unit ranges from about 0.01 to 0.03 with respect to carboxyl groups. The D.S. with respect to carbonyl groups ranges from about 0.005 to 0.01 (13). The introduction of these groups inhibits the association of the amylose or linear fraction of starch (1). Consequently, pastes of hypochlorite oxidized starch have much less tendency to gel than do pastes of the parent starch. The oxidized starches gelatinize and disperse more readily than unmodified starch to give smooth and relatively stable pastes which yield tough adherent films on drying. These properties make the oxidized starches especially useful as surface sizes and coating adhesives for paper.

The comparative viscosity ranges for different types of unmodified starches and partially depolymerized starches are shown in Figure 1 in terms of parts of water required to give about the same hot viscosity for the different starch products (19). For example, the chart shows that 40 fluidity acid-modified starch will require about 8.3 parts of water to give the same viscosity as 75 fluidity acid-modified starch in 4 parts of water.

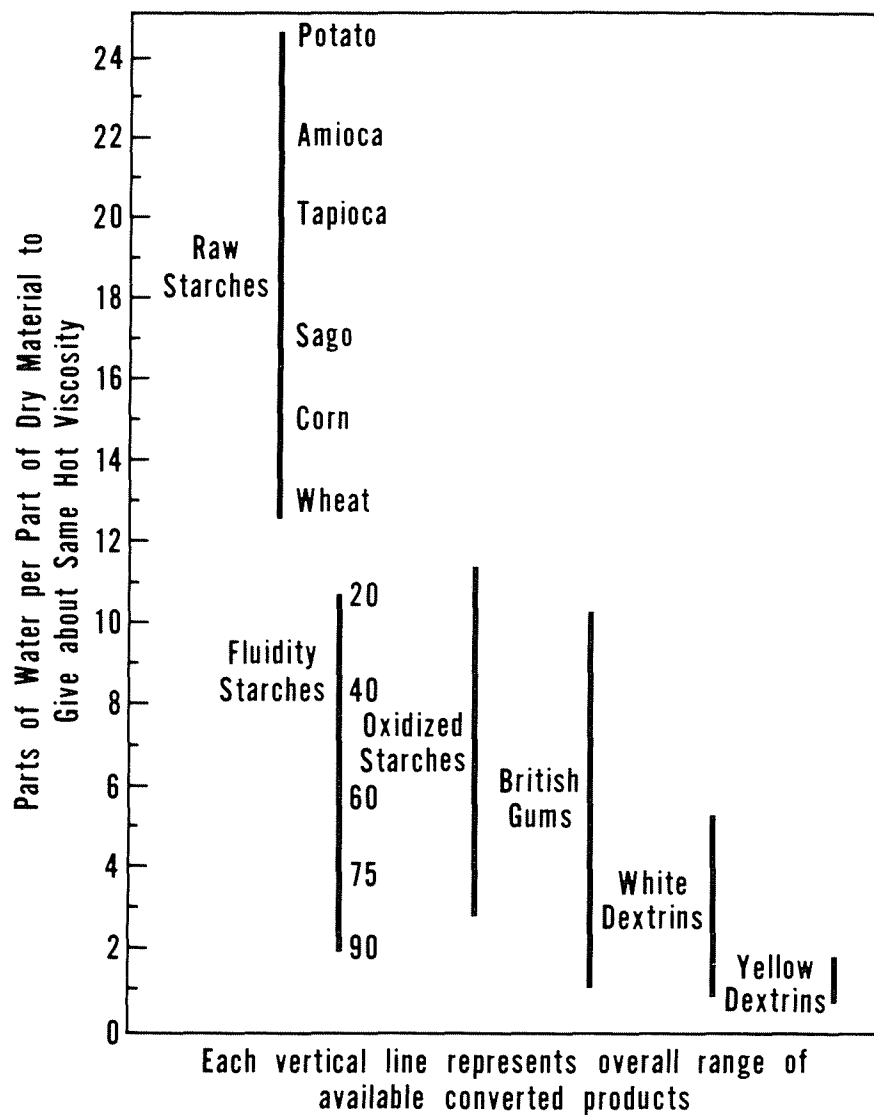


Fig. 1. Comparative viscosity ranges of different types of starches. Source: Reference 19. Reproduced by permission of the Corn Refiners Association, Inc., formerly the Corn Industries Research Foundation.

Cationic Starches

The two most widely used types of cationic starches are the tertiary aminoalkyl ethers and quaternary ammonium alkyl ethers of starch. The former are prepared by reacting starch in an aqueous alkaline slurry with either dialkylaminoalkyl chlorides or 2,3-epoxypropyl (glycidyl) tertiary amines (14). The quaternary ammonium derivatives are prepared in similar manner except that quaternary ammonium salts of either aminoalkyl chlorides or glycidyl amines are used (8). Most of the commercial grades of cationic starches have D.S. in the range of about 0.02 to 0.05. They readily disperse in hot water to give smooth, relatively stable pastes. They are especially useful in papermaking application because their positive charge makes them substantive to the negatively charged pulp fibers. They are also useful as flocculants for various types of solids suspended in aqueous systems. In addition to the cationic starches derived from unmodified starch, thin-boiling grades derived from acid-modified starches are also available commercially.

Hydroxyethylated Starches

Hydroxyethylstarch is produced by the base catalyzed reaction between starch and ethylene oxide. The D.S. in commercial grades is usually between 0.05 and 0.1 (16). Hydroxyethylstarch readily disperses on cooking in water to give pastes with good clarity and stability toward gelling on cooling. Thin-boiling hydroxyethylstarches derived from acid-modified starches are especially useful as sizing agents and coating adhesives for paper.

Pregelatinized Starch

Pregelatinized starch is prepared by drying a concentrated aqueous slurry of starch at high temperature. The most commonly used equipment for this purpose is the drum dryer or "hot-roll" (15). During heating the starch granules swell and disrupt to give, when dry, a product that is cold-water soluble. Sodium hydroxide is often added to the aqueous slurry to facilitate gelatinization. Pregelatinized starch is made mostly from unmodified starch but limited quantities of modified starches are also available in pregelatinized form. Except for their cold-water solubility, slightly lower viscosity, and less tendency to gel, properties of the pregelatinized starches are similar to those of the parent starch (15). They were developed for users who do not have facilities for cooking starch.

Applications in Paper and Paperboard

Starch and starch products are used in making paper and paperboard as wet-end additives, surface sizing agents, and coating adhesives. These terms are best explained by the brief description of papermaking which follows.

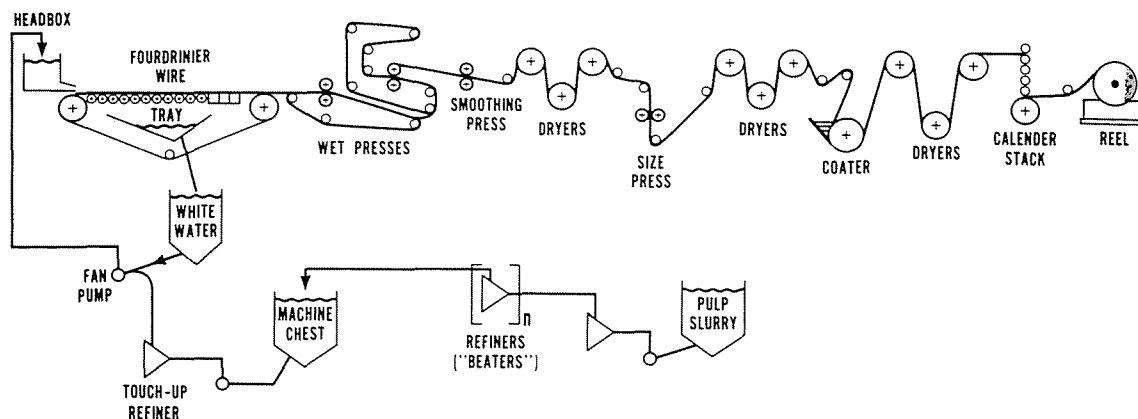


Fig. 2. Fourdrinier paper machine with size press, coater, and stock supply system.

Paper is made from cellulose fibers obtained mainly from wood. Basically, papermaking consists of removing the water from a dilute aqueous suspension of fibers through a screen to form a wet fibrous mat which is dried. Paperboard is made in the same manner except that a more concentrated suspension of fibers is used. In actual practice, two basic types of machine, the Fourdrinier² and cylinder machine, are used in making paper. Essential features of the Fourdrinier machine along with a stock supply system, a size press, and a coater are shown in Figure 2. Not all machines have a size press and coater, but machines with a size press are more common than those with a coater. Basic features of the cylinder machine are the same except for the wire section. In this machine a series of vats containing a pulp suspension is used. A wire-covered cylinder partly submerged in each vat picks up a mat of fibers as it rotates. The wet mat is pulled off the top of each cylinder as a continuous sheet. These wet sheets are brought together to form a single sheet made up of as many plies as there are cylinders.

Before paper with satisfactory strength properties can be made from pulp, it must be beaten in either beaters or refiners to bring about fibrillation and hydration. Both of these types of machines subject the pulp to vigorous rubbing between two hard surfaces. Beating or refining is generally done at 3 to 5% consistency,

²The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

consistency being the weight percent dry pulp in the aqueous suspension. Before the pulp is delivered to the head box and onto the wire (Figure 2), water is added to reduce the consistency. Depending on the type of paper or paperboard being made and the speed of the machine, the consistency at the wire ranges from around 0.3 to 0.6%.

Generally, but not always, one or more so-called wet-end additives are incorporated in the pulp suspension before paper is made from it. Wet-end additives include adhesives or bonding agents to help bind the fibers firmly together in the sheet, rosin, alum, fillers such as white clay, deflocculating agents, wet-strength resins, and dyes. Starch and modified starches are the principal bonding agents used. Other bonding agents include cellulose derivatives and natural gums such as guar gum. Addition of a bonding agent substantially reduces the amount of beating and associated power needed to give a pulp that will make a strong sheet of paper (20). The suspension of beaten pulp after dilution and addition of any required additives is referred to as the furnish. It is introduced through the headbox onto the moving wire where a continuous wet web is formed as the water drains off under the influence of gravity and suction. After further removal of water on the wet press section, the sheet is dried by passage over steam-heated rolls. If a surface size is to be applied, the sheet coming off the first drier section is passed through the size press where it is rewetted, generally with a paste of modified starch, and then redried. Depending on the type of paper being made, a clay or similar coating may be applied as discussed under the section on coating. The coated sheet is again dried, then pressed and polished by passage through a series of highly polished steel rolls called a calender stack which imparts smoothness or gloss to the paper. The calender stack may also be used to apply surface sizes and coatings to paper and paperboard. After leaving the calender stack, the paper is wound into large rolls on the reel.

Use of Starch Products in Papermaking

The consumption of starch products as wet-end additives, surface sizes, and coating adhesives is given in Table II. The 1972 figures were obtained by extrapolating the data reported (3) for 1968. For extrapolation, an average annual growth rate of 4.6% was assumed. This assumption seems reasonable because the production of paper and paperboard is reported (21) to have increased at an average annual rate of 4.6% since 1968. In 1964 the figure for all types of starches used as wet-end additives was 186 million pounds (3) which at that time would correspond to about 156 million pounds of corn starch products. In view of the estimated use of 156 million pounds of corn starches at the wet end in 1964 and the rise in paper production

TABLE II. SALES OF STARCH PRODUCTS FOR VARIOUS PURPOSES IN THE PAPER INDUSTRY

Use	Millions of Pounds of All Starch Products	
	1968 ^a	1972 ^b
Wet-end addition	96	115
Surface size	650	780
Coating adhesive	376	440
Total	1,122	1,335

^aSource: Reference 3.

^bObtained from the 1968 figures by applying an annual growth rate of 4.6%.

between 1964 and 1968, the figures in Table II for wet-end additives appear to be much too low. It is doubtful that the trend toward size-press application of starches in place of wet-end addition to upgrade strength properties of paper was in full enough force between 1964 and 1968 to explain the indicated decline in starch usage at the wet end. The trend toward size-press application was prompted by the need to reduce starch losses and minimize pollution.

Consumption data for various types of unmodified and modified starches in papermaking were reported for 1964 (3), but such data for later years do not appear to have been published. Extrapolation of the 1964 data to obtain an estimate of current consumption of corn starch products is not possible because corn starch and other starches, including potato and tapioca starches, are all lumped together in the 1964 figures. Extrapolation is further complicated by the gains that some modified starches have made at the expense of others during the 1964 to 1972 interval. However, the principal corn starch products used in papermaking will be brought out in subsequent discussions.

Wet-End Addition

The primary function of starch-based wet-end additives is that of increasing the dry strength of paper. With the exception of oxidized starches, use of starch products, particularly cationic starches, also facilitates the incorporation of inorganic fillers such as white clay and diminishes strength losses associated with the presence of fillers in paper. Unmodified starch and cationic starches are the principal starch products used at the wet end. Other starch-based wet-end additives include hydroxyethylstarch, starch lightly oxidized with sodium hypochlorite, and dialdehyde starch. The dialdehyde starch is used to impart wet strength to paper and will be discussed later. Except for special applications, starch products are thoroughly cooked in water, unless they have been pregelatinized, before addition to the aqueous pulp slurries used to make paper.

The point of addition of starch products at the wet end depends on the nature of the product, the type of paper being made, and the speed and other operating characteristics of the paper machine. This point may be at the headbox, fan pump, stock chest, beater, or any other convenient point in the stock delivery system. The amount added depends on the nature of the starch product and the type of paper being made. For unmodified starch, the addition level is usually in the range of 2 to 3% weight percent starch on a dry pulp basis. The addition level for cationic starches is usually around 0.5%. Much lower levels of cationic starch than unmodified starch are needed because the former is much more completely retained than the latter by the pulp fibers. In some mills that make heavy grades of paper and paperboard, unmodified starch or lightly oxidized starch in granule form is added to the pulp slurry. The starch is retained by physical entrapment in the wet paper mat formed on the wire of the paper machine and is gelatinized during drying of the paper. The lightly oxidized starches gelatinize more readily and are more effective than unmodified starch in this application.

Some mills are adding cationic synthetic polymers and unmodified starch at the same or different points in the wet-end system in place of cationic starch (22). The cationic polymer facilitates the retention of the starch as well as fillers, if present. The extent of this practice is not known but competition for it appears to be in the making in the form of cationic graft polymers of starch (23).

Although over 40 million pounds per year of synthetic resins are used as wet-end additives to impart wet strength to paper (3), only one starch product, dialdehyde starch (DAS), is used for this purpose. DAS is used mainly in tissue grades of paper, and its usage has never exceeded 750,000 pounds per year. DAS not only imparts high temporary wet strength to paper, but also improves dry strength properties markedly (24). Paper treated with DAS is very easy to repulp for recycling in contrast to paper treated with wet-strength resins. The high cost of DAS, engendered largely by small scale production (under 1 million pounds per year), has been the limiting factor in its use. The trend toward recycling more and more paper has revived interest in the use of DAS because of the ease with which paper treated with it can be repulped. Repulping of resin-treated paper is difficult and costly, and segregating such paper from other wastepaper is expensive. Therefore, it is believed that the market for DAS could increase markedly if it were produced on a large enough scale to reduce its cost substantially.

Oxidatively crosslinked starch xanthates (25), starch xanthate crosslinked with polyethylenimine (26), or with a polyamide-polyamine-

epichlorohydrin resin (27) all impart high wet strength and dry strength to paper. So too does hypochlorite-treated carhamoylethyl starch (28). None of these developments have been industrialized, but the more recent ones (27,28) are being actively investigated by industry.

Surface Sizing

The end use requirements for paper and paperboard dictate whether or not a surface size is applied. Surface sizing is done to improve the writing and printing characteristics, particularly ink holdout, erasability, and strength properties of the sheet. The principal starch products used in surface sizing are enzyme-converted starch, jet-cooked starch, oxidized starch, and hydroxyethylated starches.

Acid-modified starch is also used to size special grades of paper and paperboard and is usually applied at the calender stack instead of at the size press. For examples, Kraft paperboard may be sized with 60-fluidity acid-modified starch to improve its printability, and unbleached linerboard is often sized with 20 to 40 fluidity grades of the starch to increase scuff resistance (11). In the latter application, the rapid congealing properties of acid-modified starch are desirable because most of the size is retained on the surface of the sheet where it is effective as a scuff-resistant film.

Several viscosity grades of starches are needed to meet the range of surface sizing requirements. In surface sizing, a starch paste is applied to the sheet, the excess paste is squeezed out by the size press rolls (Fig. 2), then the sheet is dried. The size press roles may be in vertical configuration (one on top of the other) instead of side by side as shown in Figure 2. Paste concentrations vary depending on the type of starch product used, the desired pickup of size by the sheet, and the type of paper being sized. Usually paste concentration falls within the range of 2 to 12% solids (2). In tub sizing, a comparatively slow process conducted off the paper machine, solids content may run up to 20%. The pickup of size by the paper (weight percent starch in the sheet on a dry basis) varies from about 1 to 4% depending on the type of paper and its intended end use (29).

Oxidized starch because of the anionic character imparted to it by its carboxyl groups acts as a dispersant for clay and other mineral fillers. Oxidized starch comes off the broke (trimmings and other wastepaper) that is returned to the stock system and adversely affects retention of clay and other minerals used in making filled paper. For this reason, oxidized starch has been losing favor for the

past several years as a surface-sizing agent and is being replaced by enzyme-converted starch, jet-cooked starch, and some of the more recently developed derivatives including cationic starches (30), starch acetates (31), and cyanoethylated starches (32).

Paper Coating

Paper is coated with pigments such as white clays, calcium carbonate, and titanium dioxide to improve its printability appearance, and brightness and to increase its opacity. The same reasons for coating paperboard apply except for improvement in opacity which is adequate in uncoated boards. In order to apply pigment coatings to paper an aqueous dispersion containing the pigment, a dispersing agent for the pigment, and an adhesive must be prepared. The pigment-adhesive mix is referred to as a coating color and often contains minor amounts of additives to stabilize the coating color and improve its flow characteristics. These additives include soap which acts as a lubricant and reduces dusting of the dried coating. Detailed procedures for preparing coating colors have been published (33). Solids content of coating colors, including pigment and binder, range from about 30 to 70% depending on the weight of coating that is to be applied. Starch-based adhesives are generally used at a level corresponding to about 18 weight percent dry starch substance on a dry pigment basis. Enzyme-converted starch, oxidized starch, and dextrans as well as hydroxyethylated starches and starch acetates are used as coating adhesives (1).

To improve water resistance of coatings made with starch adhesives, materials such as a latex or urea-formaldehyde resin are used in conjunction with starch (33). However, coatings made in this way do not meet all requirements for water resistance and flexibility. Polyvinyl acetate latex, styrene-butadiene latex, and acrylic latex as well as proteins alone or in combination with crosslinking agents are used to meet requirements which cannot be met with starch adhesives (3,34).

A variety of coaters, including blade, air knife, roll, and brush coaters, have been developed for applying the coating color to paper (34). With the blade coater depicted in Figure 2, the coating color is fed into the V-shaped trough formed between the coater blade and the backing roll. Pressure between the blade and roll is adjusted to regulate the amount of coating applied to the paper as it passes through the trough of coating color and emerges between the blade and roll. To coat both sides of the paper, another coater and dryer section like that depicted in Figure 2 is provided. For paperboard, one section generally suffices because most paperboard is coated on one side only.

In high-speed coating on blade and roll coaters, the coating color is subjected to very high shear. Therefore, the rheological behavior of the coating color is a very important consideration. This subject has been reviewed in depth (34); therefore, it is commented on only briefly here. The coating color should not thicken up under the influence of high shear. On the other hand, it should not thin out too much and allow the adhesive to strike too deeply into the sheet leaving the surface coating deficient in adhesive.

Use of Starch in Adhesives

The major use for starch-based adhesives is in so-called converting processes applied to paper and paperboard. These processes include fabrication of corrugated boxboard, paper bags, folding cartons, laminated paperboard, and spiral-wound tubes as well as off-machine pigment coating of paper and making of gummed labels and tapes. Off-machine coating refers to coating paper after it is made in distinction to coating the paper as it is being made on the paper machine. In 1968, 350 million pounds of starch products were used as corrugating and laminating adhesives (3). Application of the previously mentioned 4.6% annual growth rate (Table II) to the 350 million figure brings it up to 420 million for 1972. The estimated consumption of starch products in other converting operations in 1969 was 500 million pounds (3). However, this figure is for corn starch and all other starches. Adjustment of the figure to a corn starch base brings it down to around 450 million pounds. This figure increases to 513 million for 1972 if the 4.6% annual growth rate is applied.

Starch products used in adhesives include unmodified starch, dextrins, hydroxyethylated starches, oxidized starch, waxy maize starch, acid-modified starch, and starch acetates (6,12,13,16,31). Data on the annual consumption of individual starch products in adhesives are not available nor is information on the amount of starch products used in any one adhesive application available.

Starch-based adhesives are supplied either as dry powders or ready-to-use liquids depending on the stability of the formulations. Powdered adhesives are available in either cold-water-soluble or hot-water-soluble forms. In addition to starch products, adhesives often contain alkali, borax, plasticizers, defoamers, and preservatives (6). Many different adhesive formulations ranging from fairly simple to complex have been developed to meet requirements for making a wide variety of products. It is not the purpose of this review to cover all of these many and varied aspects of adhesives, but rather to discuss a few selected applications illustrative of the use of different types of starch-based adhesives.

Corrugated Board

Regular corrugated board consists of one corrugated or fluted medium and two liners or facings. However, only one liner or facer is used sometimes (35). Starch is the most widely used adhesive employed in gluing the linerboard to the fluted medium. The adhesive consists of a cooked paste of a so-called carrier starch, usually unmodified starch, containing sodium hydroxide and borax in which is suspended unmodified starch in granule form. The concentration of the carrier starch in the mix is about 3 weight percent and that of the starch in granule form about 18%. The paste of carrier starch serves to keep the starch granules from settling. The sodium hydroxide and borax are used to lower the gelatinization temperature of the granular starch and to increase tack and adhesive strength. This adhesive is not stable enough to be sold in liquid form. It must be made from the solid ingredients at the plant where it is being used. In making corrugated board, the adhesive is metered onto the peaks or ridges of the fluted medium, then the linerboard is applied, followed by application of heat and moderate pressure. The starch gelatinizes immediately and firmly bonds the assembly together before it passes off the corrugating machine to the storage area. If a double-faced board is to be made, the second liner is applied in the same manner.

Paper Bags

The type of adhesives used in making paper bags varies according to the type of seal and the kind of bag being made. This is best illustrated by the different starch-based adhesives used in making grocery bags and multiwall paper sacks.

The side-seam adhesive for grocery bags may be made from oxidized starch, acid-modified starch, or a dextrin to which borax, soda ash, and metasilicate are added (36). Solids content in the adhesive ranges from 20 to 30%. The bottom pastes may be derived from a mixture of starch and dextrin, or from acid-modified starch, or from oxidized starch to which caustic, clay, soap, tallow, and other minor ingredients are added. Solids content in bottom pastes ranges from 15 to 25% depending on the type of starch product and other additives used (36).

In the fabrication of multiwall paper sacks, the plies of paper are first glued together by the cross-pasting unit which applies an intermittent line of glue to each ply. The adhesive used should be tacky and quick setting. Modified starches and dextrans to which a mineral filler is often added are used as cross-pasting adhesives. Solids in this type of adhesive range from 25 to 33% (6). For side-seam gluing, the glue may be slow drying but must have fast initial tack and is usually made from acid-modified starch or white dextrans

(6). Acid-modified starches are used extensively in the preparation of adhesives for sealing the bottom of multiwall bags. With modern roll-type applicators, solids content of the adhesive is about 20% (6). Resins such as urea-formaldehyde are often added to bottom adhesives as well as side-seam adhesives to provide water resistance (36).

Gummed Paper

Envelope seals are probably the most familiar example of gummed paper. Envelope seals are made from aqueous pastes of highly soluble dextrans. Solids concentration in these pastes ranges from 55 to 65% (36). A nonhumectant type of plasticizer is an important ingredient in the pastes; it prevents curl and keeps the adhesive film from crazing. If a humectant type of plasticizer were used, the seals would stick together in humid weather when the envelopes were packaged.

Back seams for envelopes require a different type of adhesive. This adhesive should be slower drying than the seal adhesive with some wet-tack and no color show-through. For this purpose highly soluble types of white dextrans are usually used along with a plasticizer such as urea (36).

Other Applications

In addition to the uses just discussed, starch-based adhesives are used in making spiral-wound tubes, laminated paperboard, and cardboard boxes. They are also employed in gluing paper coverings to cartons and as packaging seals. Nonpaper-related uses include bonding agents for foundry cores, insulating boards, and acoustical tile. In the last two items together, 155 million pounds of starch products were used in 1972 according to starch suppliers.

Textile Applications

The principal use for starch products in the textile industry is as a warp size to strengthen warp yarns and improve their resistance to abrasion during weaving. Starch products are also employed in the finishing of fabrics, in printing, and as components in finishes for glazing sewing thread (5). The last two applications are of a minor nature and will not be discussed here. The use of starch in printing pastes was a significant application when large amounts of water-dispersible dyes were employed, but starch was largely replaced by resins when insoluble pigments were introduced as printing agents (1).

The principal starch products sold to the textile industry are listed in Table III. Unmodified starch is used in finishing

TABLE III. SALES OF PRINCIPAL STARCH
PRODUCTS TO THE TEXTILE INDUSTRY

Starch Product	Millions of Pounds in 1972 ^a
Unmodified starch	83
Acid-modified	170
High-amylose	22
Total	275

^aData were obtained from starch suppliers.

operations, but it is not a satisfactory warp size and is modified at the mill to reduce its viscosity. The processes commonly used for this purpose are: conversion with enzyme, steam-jet cooking, and the subsection of cooked pastes to high shear in a specially designed homogenizer (5). Other starch products used by the textile industry in addition to those listed in Table III include starch acetates, hydroxyethylated starches, oxidized starch, and dextrans (1,12,13, 16,31). Information on the amounts of these starch products currently used could not be obtained.

According to information received from starch suppliers, the amount of starch used by the textile industry has been declining at an annual rate of 5 to 6% for the past few years. This decline is probably largely a reflection of further gains by carboxymethyl-cellulose and polyvinyl alcohol which were adopted as warp sizing agents several years ago. These polymers have lower 5-day biological oxygen demand (BOD) than starch and, therefore, when discharged into streams or rivers do not deplete the oxygen in the water as rapidly as does starch (1). The replacement of traditional starch products with new starch derivatives such as the sulfo-succinic acid half ester of starch (37), which do not need to be applied at as high a level as traditional starch products, also contributes to the decline in the market for starch in textile applications. Unfortunately, data on the volume of the more effective starch products used are not available.

Warp Sizing

Warp yarns are sized to enable them to withstand abrasion associated with the weaving process. The warp yarns are the yarns between which the shuttle carrying the weft threads passes during the weaving operation. The process of sizing is often called

slashing. Yarns spun from staple fibers such as cotton are slashed with pastes which contain about 9% by weight of a starch product of appropriate viscosity and about 0.5% of a softening agent (5). In the slashing operation, the strands of yarn are lined up side by side and passed through the size solution followed by passage through squeeze rolls to remove excess size. The wet yarn is then dried on steam-heated rolls. With traditional starch-based sizing agents, the amount of size added to spun yarns is usually 10 to 15% on a dry weight basis (5).

Materials used to size yarns composed of continuous filaments must penetrate the yarn completely (5); therefore, relatively low-viscosity starches are required. About 3 to 5% of size on a dry weight basis is added to filament yarns (5).

After fabric is woven it is desized by treatment with aqueous solutions of alkali or enzyme followed by washing with water.

Ordinary starch products are not satisfactory for sizing synthetic fibers or glass fibers. For these applications, high-amylose starches as well as synthetic polymers are used. The high-amylose starch products include the unmodified starches with about 60% and 70% apparent amylose content as well as cationic and hydroxypropyl derivatives of the starches. Information on the amounts of each of these starch products used is not available.

Textile Finishing

Both unmodified and modified starches are employed in textile finishing processes to increase the stiffness of fabric, to change the hand (feel) of the fabric, and to improve appearance by filling in the interstices of the weave (5). To increase stiffness and improve hand, the fabric in the last stages of finishing is passed through a dilute paste of starch product, then it is run through squeeze rolls to remove excess paste followed by drying on steam-heated cylinders. In filling operations, a starch paste containing filler such as talc or clay is often used. If permanent properties such as crease resistance are desired, synthetic polymers or mixtures of synthetic polymers and starch are employed (7).

Miscellaneous Applications

Miscellaneous applications for starch products include their use as flocculating agents, anticaking agents, mold-release agents, dusting powder, binders for pharmaceutical products (tablets and pills), thickening agents, and as raw materials in the production of chemicals and explosives.

Developmental Products

In addition to the developmental starch products mentioned in the section on papermaking, a number of other products have been developed which have considerable industrial potential. These are anionic and cationic graft polymers of starch (38,39) and starch-based reinforcing agents for rubber (40-42), as well as agents which enable powdered rubber to be made readily and inexpensively from latex, the form in which natural rubber and most synthetic rubbers are first obtained (43,44).

Anionic graft polymers made by the saponification of starch-polyacrylonitrile graft polymers are exceptionally powerful thickening agents for aqueous and certain aqueous-organic systems (39). Cationic graft polymers of starch made by cografting acrylamide and various aminoacrylates to starch are very effective flocculating agents for several types of finely divided solids suspended in aqueous systems (39,45,46).

Incorporation of crosslinked starch xanthate into rubber reinforces the rubber to about the same degree as do medium grade carbon blacks (40). The starch product is incorporated into the rubber by adding starch xanthate of DS 0.06 to 0.10 to latex, followed by addition of an oxidant and acid. The oxidant converts the xanthate to the insoluble xanthide (oxidatively crosslinked xanthate) which coats the rubber particles and coprecipitates with them under the destabilizing influence of the added acid (40-42). In the early stages of this developmental work, the coprecipitate of starch xanthide and rubber was obtained as large curds which were consolidated for subsequent processing and curing. Subsequently, it was discovered that these large crumbs could be granulated or powdered in a hammer mill without chilling the crumbs with liquid nitrogen as is necessary in grinding conventional rubber crumbs (43). In the latest development, powdered rubber has been obtained directly from starch xanthate-latex mixtures by adjusting the rate of stirring and other variables during the crosslinking and coprecipitation stages to give finely divided particles (44). In this process, the wet particles were washed with alcohol before drying. It now appears that the alcohol wash can be eliminated.

The development of an economical process for making powdered rubber has been a long-sought goal of the rubber industry because powdered rubber like powdered plastics can be injection molded or extruded without prior high-shear milling to give good quality finished products. In addition to savings in processing costs, the availability of powdered rubber would considerably reduce the capital investment needed for processing equipment (47).

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